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Evaluation of 3M Empore™ Rad Disks for Radium Determination in Water

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Evaluation of 3M Empore™ Rad Disks for Radium in Water

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Abstract

Empore™ Radium Disks, manufactured by the 3M Corporation, have been evaluated for use in EML's Quality Assessment Program (QAP) for the rapid determination of Radium in Water. These 47 mm diameter by 500 μm thick membrane disks are impregnated with a crown ether that selectively extracts β-emitting ^{225}Ra ($t_{1/2}$ = 14.8 dy) or ^{228}Ra ($t_{1/2}$ = 6.7 yr) and α-emitting ^{223}Ra ($t_{1/2}$ = 11.2 dy), ^{224}Ra ($t_{1/2}$ = 3.6 dy) or ^{226}Ra ($t_{1/2}$ = 1622 yr) from water. Typically, the Ra bearing solution is loaded onto the disk from 2N HNO_3 and eluted with 0.25M (basic) ethylenediamine tetraacetic acid (EDTA). Using 10-20 mL amounts of non-acidified matrix free samples, we pre-conditioned each disk with 2N HNO_3 and individually measured the retention and elution characteristics of 20 isotopes that are constituents of EML's QAP samples. We utilized either (1) Liquid Scintillation Analysis (LSA), (2) NaI(Tl) gamma counting or (3) Solid State Alpha Spectrometry to make our measurements, rather than ^{222}Rn emanation, which is specific only for ^{226}Ra. We found that the disks could be counted directly (for ^{226}Ra) using a low background gas-proportional α/β counter, with 10% α-counting efficiency, or by LSA, with 99% α-counting efficiency. The 6 α-emitting actinides tested were ^{230}Th, nat U, ^{242}Pu, ^{243}Am, ^{237}Np and ^{244}Cm. We selected several β/γ-emitting Group I (^{3}H, ^{40}K, ^{137}Cs) and Group II (^{45}Ca, ^{90}Sr/Y, ^{133}Ba) elements as potential interferents when measuring Radium by LSA. Three transition elements (^{55}Fe, ^{54}Mn, ^{106}Ru/Rh) as well as ^{226}Ra and 2 of its β-emitting progeny, ^{210}Pb and ^{210}Bi were individually tested. We found that ^{210}Po and ^{210}Bi, were not retained by the disk while > 95% of added ^{226}Ra was recovered from samples that we tested. The only other divalent elements that eluted with EDTA were Pb (90% eluted), Sr (85%) and Ba (20%). For three QAP water samples spiked with 40 dpm (0.6 Bq) of ^{226}Ra, the found to added ratio was 0.90 $\pm$ 0.14. The 20 mL QAP samples (acidified with 1N HCl) contained ^{3}H (300 dpm), ^{55}Fe (99 dpm), ^{90}Sr/Y (1.8 dpm) ^{238}Pu (2.2 dpm), ^{241}Am (1 dpm), ^{54}Mn (51 dpm), ^{60}Co (42 dpm) and ^{137}Cs (54 dpm). For rapid screening , good results were obtained following a 15 min LS count of either the unstripped 3M disk or EDTA fraction. Low-level samples containing < 2 dpm (0.03 Bq) were below the LLD of our LS counter and required a direct α-count of ^{226}Ra. This was accomplished by microprecipitating Radium (as $Ra/BaSO_4$) at pH 4-5 from the EDTA fraction, following Sill's method. A first attempt to measure Radium in New York City tap water was unsuccessful because of the presence of gram amounts of soluble NO_3 salts that presumably interfered with ^{226}Ra extraction. Because the Radium concentration in NYC water is extremely low (0.4 mBq L^{-1}), we evaporated 50 L to 100 mL. Prior to pre-filtering with glass-fiber pads, we wet ashed with concentrated HF, HCl and finally HNO_3. Following an 18 h count, we were unable to detect a ^{226}Ra α-peak in the EDTA strip fractions of 4 pre-filtered and concentrated NYC water samples, one of which was internally spiked with 3 dpm of ^{226}Ra. In each case, we accounted for 86-95% of γ-emitting ^{133}Ba that was added as a yield tracer just prior to microprecipitation. We were, however, able to recover 95% of 10 dpm ^{226}Ra added to 2 L of NYC water samples measured by either LSA (without ^{133}Ba) or alpha spectrometry.

INTRODUCTION

This report evaluates a new commercially available membrane disk, Empore™ (3M Corportion), that separates waterborne β-emitting ^{225}Ra ($t_{1/2}$ = 14.8 dy) or ^{228}Ra ($t_{1/2}$ = 6.7 yr) and α-emitting ^{223}Ra ($t_{1/2}$ = 11.2 dy), ^{224}Ra ($t_{1/2}$ = 3.6 dy) or ^{226}Ra ($t_{1/2}$ = 1622 yr) from potentially interfering elements. At the Environmental Measurement Laboratory (EML), six methods exist for the determination of Radium (HASL-300). Most rely on the ^{222}Rn emanation procedure, which is specific for ^{226}Ra. The 3M product was designed to eliminate most of the steps in the Environmental Protection Agency's (EPA) method 903.0 for Radium in water (Kreiger 1980) which also relies on ^{222}Rn emanation. Each methodology entails several precipitations and separations followed by a 7-8 day ingrowth time for ^{222}Rn. Approximately 75% of maximum ^{222}Rn ingrowth is achieved after 7.8 days (i.e., two ^{222}Rn half-lives). Recently, 3M marketed a 2" disk capable of extracting Ra isotopes from 1 L aqueous solutions in 20 minutes (3M 1995). The 3M Empore™ Radium Rad disks were the 3rd in a series of solid phase extractant (SPE) products that also include Sr and Tc Rad Disks.

The effective thickness of the 47 mm diameter by 500 μm thick Ra membrane disk, weighing 0.430 g $\pm$ 1% , is 25.2 mg cm^2. The disk contains a crown-ether, covalently bound to inert substrate particles, that selectively extracts Ra^{+2} from acidic solutions. A crown-ether is a 20-25 atom carbon-oxygen donut-like molecule with a unique size/charge selectivity.

The 3M Radium extraction procedure consists of first mounting the 2" disk on a Millipore™ vacuum filtration system. In this configuration approximately 55-65% of the total disk area is utilized. The manufacturer recommends that the Radium bearing sample be acidified to 2N with Nitric acid. The sample is then vacuum suctioned through the disk and

washed with 2N Nitric acid. Radium may be stripped using 0.25M EDTA (Ethylenediamine tetraacetic Acid: FW = 292.3 g $Mole^{-1}$). Specific Radium isotopes may be determined by separation and counting of their respective progeny (i.e., ^{228}Ac for ^{228}Ra and ^{222}Rn for ^{226}Ra).

The goals of this project were : (1) to determine if the 3M Rad disks could be integrated into EML's QAP (Quality Assessment Program) testing protocol for ^{226}Ra, (2) to determine the limitations of the disk and (3) to investigate other direct measurement techniques for α/β-emitting Radium , rather than ^{222}Rn emanation (which is specfic only for ^{226}Ra). To evaluate the product, we used (a) selected matrix-free radio-tracer solutions, (b) a QAP water sample (containing mixed radionuclides with ^{226}Ra), and (c) New York City tap water.

Twenty NIST (National Institute of Standards and Technology) traceable radioisotopes were tested for their binding capacity to the 3M disk. These included ^{226}Ra (in equilibrium with its' progeny: ^{210}Pb, ^{210}Po, and ^{210}Bi) as well as ^{210}Pb(with ^{210}Bi/Po) and ^{210}Bi(with ^{210}Po) that were each tested separately. Gamma emitting ^{207}Bi was used to validate the ^{210}Bi results, using Cerenkov counting of the 1.160 MeV beta of ^{210}Bi. Also tested were 3 alkaline earth elements (^{45}Ca, ^{90}Sr/Y, ^{85}Sr, ^{133}Ba), chosen for having the same di-valent charge as Ra and 3 Group I elements (^{3}H, ^{40}K, and ^{137}Cs), chosen for their mono-valent charge. Six Actinides [^{244}Cm(III), ^{243}Am(III), ^{242}Pu(IV), nat U, ^{230}Th(IV) and ^{237}Np(V)] were selected because several of them are constituents of EML's QAP water samples. If any co-extract with Ra, then they could be potential interferents, depending on the method of radiation measurement. The transition elements ^{106}Ru/Rh, ^{54}Mn, and ^{55}Fe were also tested as possible interferents as well as ^{14}C. The properties of the nuclides used in this work are shown in Table 1 whereas the decay schemes

of ^{223}Ra through ^{226}Ra are shown in Fig. 1.

Literature Summary

To date, the only published literature is from cooperative work performed by Kinney/ Shannon, Smith/ Orlandini, and Hoffman/ Seely at PACE, Inc. , Argonne National Laboratory and 3M Corporation, respectively (Kinney 1995). Data by Orlandini and Smith showed that ^{226}Ra could be loaded onto the 3M disk from either DI water (96% uptake) or <8 N HNO_3 (95-99% uptake). They also showed that Ra uptake was markedly affected by 10,000 ppm of NH_4^+ or Mg^{+2} in a 0.1N HNO_3 load solution. No effect was obseved with 10,000 ppm Ca^{+2} or 10 ppm Pb^{+2}. A 15% reduction in Ra uptake was observed with 10,000 ppm of Ba^{+2} and Na^+. Since the nominal Ba^{+2} capacity of the Ra Rad disk was estimated to be about 500 ug, the use of stable Ba for yield determinations would not seem practicle.

About 90% of extracted Ra is eluted (stripped) from the disk with 5 mL of 0.25M EDTA and 96% eluted with 10 mL of EDTA. Using 250-1000 mL volumes of either spiked lake, well and municipal water samples, 88-98% of added ^{226}Ra was recoved from the disks. For ^{228}Ra analyses, the average recovery of spiked 50 mL water samples was 94.1%. Preliminary results suggested that ^{222}Rn, the progeny of ^{226}Ra could be measured by LSA using a mineral based cocktail (DuPont NEN 957A) following a 3 day ingrowth time. Using 1000 pCi (2200 dpm) of ^{226}Ra in 50 mL and 25 mm disks, the method MDA was estimated to be 11 pCi L^{-1} (24 dpm L^{-1}) which is a factor of ten greater than the EPA method detection limit of 0.2 - 1 pCi L^{-1} for ^{226}Ra. It was suggested that the EPA detection limit could be achieved if a 500 mL sample were loaded onto a 47 mm disk followed by a 30 min LS count.

METHODS AND RESULTS

Instrumentation

The ^{222}Rn emanation procedure was not used in this evaluation. Rather, several alternative a counting methods, compatible with Radium Rad disk extraction procedure, were investigated. The primary counting method utilized a commercially available Packard Tri-Carb 2250CA Liquid Scintillation Analyzer (Packard Co , Downers Grove, IL) in combination with Insta-Gel-XF cocktail. The LS detection system was used to measure both the alpha (α) and beta (β) activity contained in the eluates and disks. As a screening method (for large numbers of samples), LSA techniques offer advantages over those based on α-spectrometry with a disadvantage of poor energy resolution (i.e., 300 keV FWHM)(Blackburn and Al-Masri 1992). The LS techniques used in this work have the advantage that ^{226}Ra α-activity is measured directly and not through it's progeny as with other methods. However, the α-radiations of ^{223}Ra (5.71 MeV) and ^{224}Ra (5.68 MeV) are not resolvable by LSA. The detection efficiency of the LS counting system is $>$ 98% for α-emitters and $>$ 90% for β's with E_{max} $>$ 300 keV (Passo 1994, Scarpitta and Fisenne 1996). Beta emitting ^{228}Ra (0.03 MeV E_{max}) cannot be measured by LS techniques whereas ^{225}Ra (0.360 MeV β-max) can. When performing Cerenkov counting, a wave-shifter may be added to the aqueous sample to enhanse the LS detection efficiency. The Cerenkov efficiency in water is typically 42% per MeV β-energy above the 0.263 MeV Cerenkov threshold. Alpha emitters are not detected by Cerenkov radiation. For gamma (γ) emitters, a Harshaw NaI(Tl) crystal interfaced to a multichannel analyzer, was used. The disks were also counted for retained activity using a low background α/β gas proportional counter (Tennelec LB4110). For low level measurements, such as NYC tap water, α-emitting ^{226}Ra

was directly measured by alpha spectrometry using EML's 300 mm^2 solid-state surface-barrier detectors (HASL-300). These detectors, with a 50 keV FWHM resolution (using $BaSO_4$ precipitates), are 35% α-efficient.

Instrument Calibration

The LSA had been previously calibrated (Scarpitta and Fisenne 1996) using most of the 20 isotopes used in this study. Appendix-F1 shows 3 spectra obtained using either α, β or γ/Auger emitting elements (^{226}Ra, $^{90}Sr/Y$, ^{133}Ba). Appendix-F2 shows the LS detection efficiencies as a function of β-energy. Appendix-F3a shows the positions of the α-peaks in un-quenched LS samples whereas Appendix-F3b shows α-peak shifting , due to quenching. For the LS phase of this study, 2 efficiency/quench calibration curves were established for ^{226}Ra using a NIST traceable ^{226}Ra standard that was diluted into successively decreasing activity concentrations. This was done by sequential one to one serial dilutions, ranging from 100 to 1.5 dpm (disintegrations per minute). The 168 dpm g^{-1} master ^{226}Ra solution (2.8 Bq g^{-1}) contained 1.9 mg of $BaCl_2$ per gram of 1.4M HCl solution. Insta-Gel-XF cocktail was then added and the calibration samples counted for one hour in the LSA with both a full and 50-700 keV α-region of interest (ROI). Figure 2 shows the two efficiency vs activity calibration (cpm/dpm) curves for a quenched ^{226}Ra solution. The calibration curves shown are for samples containing ^{226}Ra (with progeny) in 10 mL water + 10 mL Insta-Gel XF at 2 window settings.

When using the full-window, the LSA's efficiency (i.e. slope) for ^{226}Ra + progeny was found to be 2.76 cpm/dpm or 276%. Using a narrower α-ROI, the efficiency was 194%. With a full-window, the approximately 300% efficiency suggests that three elements are present:

^{226}Ra, ^{210}Po, and ^{210}Pb. When the full-window was reduced to 50-700 keV, β-emitting ^{210}Pb was excluded. Hence, two α-emitting elements, ^{226}Ra and ^{210}Po, contribute to the 200% efficiency in Figure 2. When ^{226}Ra tracer is added to a sample, ^{222}Rn, the progeny of ^{226}Ra, degasses. This breaks the equilibrium that exists between ^{226}Ra and its progeny in the sample. Without ^{222}Rn support, the short-lived progeny (See Fig 1.) decay quickly, leaving only the long-lived progeny of ^{226}Ra (^{210}Bi, ^{210}Po, and ^{210}Pb).

For our purposes, it was <u>not</u> necessary to calibrate the γ counter for absolute efficiency (cpm/dpm) due to the ease of taking a total count for any sample before and after any test process. All γ measurements and calculations were performed by taking a ratio of measured counts to total counts. When testing γ-emitters (^{85}Sr, ^{133}Ba, ^{137}Cs and ^{207}Bi), a counting geometry correction was required when we counted the disk directly on the surface of the 3 " diameter NaI(Tl) detector following each elution step. The correction factor of 0.421 was determined by adding a known amount of γ activity to a Ra disk, which was then counted in a petri dish placed on top of the NaI(Tl) crystal. The disk was then rolled up and placed in a plastic tube, and recounted inside the 1" diameter by 2 " deep well of the NaI(Tl) crystal.

Initially, every disk was gross α/β counted following the addition of the load, wash and strip solutions. Using ^{226}Ra spotted on 2" diameter styrofoam pads, the α-efficiency of the Gross α/β counter was about 30%. When ^{226}Ra was spotted onto the Empore™ Rad Disk, the α and β efficiencies were reduced to 10% and 15%, respectively. The 20% drop in efficiency was due to attenuation of the ^{226}Ra (and progeny) α/β -particles within the 500 μm thick disk.

For QAP apllications, gross α/β counting of the disk was not a feasible way of making low-level ^{226}Ra measurements due to the 10% α-detection efficiencies. LSA, with >98% α-

counting efficiency found to be adequate for ^{226}Ra levels > 10 dpm (4.5 pCi or 0.166 Bq), with Alpha Spectrometry being the only alternative (besides ^{222}Rn emanation) for activites < 10 dpm. The only α-emitting actinides (if present in an electroplated sample) that would interfere with ^{226}Ra determination by α-spectrometry are ^{230}Th, $^{233,234}U$, ^{237}Np and ^{242}Pu (See Appendix F-4). For ^{223}Ra (6.3 MeV-α) and ^{224}Ra (5.4 MeV-α), only ^{236}Pu and $^{243,244}Cm$ would interfere if present in a sample. However, the presence of 1.46 g of EDTA in the 20 mL strip fraction prohibits direct α-counting of the evaporated sample, due to self-absorption of the 4.78 MeV ^{226} Ra alpha. This problem (and that of α-emitting actinides) is avoided by microprecipitating Ra with $BaSO_4$.

The Lower Limit of Detection (LLD), at the 95% confidence level, was determined from multiple background counts (NCRP No. 97). For a one hr LS count, it was found to be 2.5 cpm and 1.4 cpm for the full and α-window, respectively. The LLD of EML's α-spectrometers was previously determined to be 0.01 cpm for a 16 hour count (HASL-300/Ra-05) using $BaSO_4$ blanks.

Individual Isotope Retention

In determining the efficiencies with which ^{226}Ra and twenty other α, β or γ emitting elements are eluted or retained by the disk, we deviated slightly from 3M's protocol. Rather than loading, washing and striping with 20 mL volumes, we used 10 mL aliquots for compatibility with LS counting. Reduced elution volumes affected the extraction efficiencies by 5-10% whereas loading from DI water affected the extraction efficiencies by 4% (Kinney etal. 1995). Approximately 3000-6000 dpm of each nuclide were loaded from DI water onto to a

fresh disk pre-conditioned with 2N HNO_3. The eluates were directly counted using a NaI(Tl) gamma well counter for γ-emitters (^{85}Sr, ^{133}Ba, ^{207}Bi and ^{137}Cs) or by LSA for the α/β-emitters (Nat U, ^{243}Am, ^{45}Ca, etc.) (see Table 1). In 3 cases (Cs, Sr and Ba), duplicate extractions were performed and were within 4% of each other.

The results in Figures 3a and 3b show that the 3M disk performed extremely well, with minimal retention (< 6%) of the Actinides and Group I elements. The ^{226}Ra was stripped with >95% efficiency using 10 mL of 0.25M EDTA. Bismuth and Polonium, the progeny or ^{226}Ra were not retained by the disk. The only other elements eluting with EDTA were: (1) Ba (20% stripped), (2) Sr (85% stripped), and (3) Pb (90+% stripped). These divalently charged elements, with ionic radii ranging from 1.00 - 1.40 Angstom, could interfere with ^{226}Ra measurements and/or binding, if present in large (i.e., mg) quantities. Using ^{90}Sr in equilibrium with its progeny, ^{90}Y, 35% of the total counts added (or 70% of progeny activity) eluted in the load and wash solutions as ^{90}Y, with a small percentage in the 10 mL EDTA strip solution. After stripping, 40% of added ^{90}Sr was retained on the disk.

We further investigated whether the disk could be counted directly in a LSA for retained Ra activity, without stripping the Ra off the disk. This was done by spiking a nitric acid conditioned disk with 177 dpm of ^{226}Ra that contained its progeny, ^{210}Pb, ^{210}Po and ^{210}Bi. The load, wash and strip fractions were counted in the LSA using 2 preset windows (0-50 keV for low energy βs and 50-700 keV for αs). The data in Figure 4a show that both ^{210}Bi and ^{210}Po are not retained on the disk after loading and washing. Both β-emitting ^{210}Pb and α-emitting ^{226}Ra were eluted from the disk, with virtually total recovery of added ^{226}Ra (i.e. 177 dpm). Approximately 10% of the total added activity (cpm) remained on the disc after stripping. To

determrmine that component, a separate experiment was performed where 10,000 dpm of ^{226}Ra was loaded onto a fresh disk and stripped with EDTA. The disk was then added to 10 mL of Insta-Gel XF and counted repeatedly for 3 hours and then 3 times over a 30 day period. The data in Figure 4b clearly demonstrate that 11% retention of added activity was due to ^{210}Pb ($t_{1/2}$ = 22 y) and not ^{226}Ra. Had ^{226}Ra been retained by the disk, then progeny ingrowth would have occurred during the 30 day time period after which the disk was stripped with EDTA. We conclude that the 3M Ra Rad disk **can** be directly LS counted for ^{226}Ra, provided one uses a sufficiently narrow α-ROI to eliminate counts from β-emitting ^{210}Pb that may be present on the disk.

QAP Sample Testing by Liquid Scintillation Analysis

We next evaluated the 3M Rad disk using an EML QAP sample spiked with ^{226}Ra. The purpose of this test was to determine the ^{226}Ra extraction efficiency of the disk in the presence of α and β-emitting radionuclides (see Table 2) that are constituents of the QAP water samples. A 40 dpm spike of ^{226}Ra was added to 20 mL of QAP water (^{133}Ba was not added as a yield tracer). The acidified (1N HCl) QAP sample was loaded onto the disk, washed with 20 mL 2N Nitric acid and ^{226}Ra stripped using 20 mL of 0.25M EDTA. Each of the fractions were then evaporated to 10 mL in 20 mL borosilicate glass LS vials, after which 10 mL of Insta-Gel was added to each fraction. Triplicate samples, including the disk, were counted for fifteen minutes in the LSA with a 1 sigma error of $<4\%$. A QAP water that **did not** contain the ^{226}Ra spike was included as a sample ' blank'.

The results of the analysis are shown in Table 2. Using a ROI of 50- 700 keV, and

subtracting out the instrument background contribution, there were more than 40 cpm (counts per minute) in the replicate EDTA strip solutions. The strip solution of the QAP 'blank' (i.e., no ^{226}Ra spike) contained 7 cpm above instrument background. After subtracting out the 7 cpm from the 40+ cpm observed in our QAP sample, 90$\pm$14% of the added ^{226}Ra was accounted for in the strip solution (see Table 2, column 7). We conclude that for a Ra/Sr ratio of about 10:1 (or greater), the 3M Ra Rad disk can be utilzed for a rapid determination of ^{226}Ra contained in QAP water (without use of a yield tracer).

^{226}Ra in Tap Water- Alpha Spectrometry

We finally tested the disk using a real-world sample. We chose NYC tap water, using a previously established mean value of 0.41 $\pm$ 0.09 mBq L^{-1} (Fisenne 1987) to compare our data to. Because the ^{226}Ra levels are extremely low in tap water, we concentrated 50 L of water into about 100 mL. The samples were wet ashed by repeated applications of concentrated HF, HCl and finally HNO_3 . The samples were then pre-filtered through glass-fiber pads to remove any other solids, and then passed through the 3M extraction disk. The ^{226}Ra in the EDTA strip fraction was then microprecipitated as $Ra/BaSO_4$ using Claude Sills' method (Sill 1987). The method of Sill requires a $Ra/BaSO_4$ microprecipitation at pH 4-5 in DTPA where elements that form insoluble sulfates precipitate out. Using Sills' method, we were able to simultaneously microprecipitate both ^{226}Ra and ^{133}Ba from both DTPA or EDTA solutions (Figure 5). These $Ra/BaSO_4$ microprecipitations were approximately 95% efficient using 1" diameter 0.1 μm Metricil^R filters (Gelman Scientific, Inc). When measuring NYC tap water, a known amount of ^{133}Ba was added as a yield tracer just prior to microprecipitation. The NYC tap water was

measured in triplicate and once with an internal spike containing 3.3 dpm ^{226}Ra. A reagent blank was prepared from 50 L of evaporated DI water.

The results were inconclusive (See Table 3). After correcting for α-detector efficiency (35%) and Ba-133 microprecipitation yield (85%), one of the samples yielded a net activity of 0.3 mBq L^{-1} which was comparable to Fisenne's average value of 0.41 mBq L^{-1} of ^{226}Ra. However, we did not observe a ^{226}Ra peak in each of the 3 NYC water samples, so we could not be sure that the observed counts were ^{226}Ra. The absence of ^{226}Ra in the internally spiked NYC sample confirmed that the disk did not extract added ^{226}Ra from pre-filtered and preconcentrated NYC tap water. The most likely reasons for this were (1) the presence of large amounts of dissolved salts which interfered with Ra extraction or (2) loss of Ra in the pre-filtered residues.

Table 4 (to Follow) shows the results of 2 NYC tap water samples to which 10 dpm of ^{226}Ra was added. The 2L samples were loaded onto HNO_3 pre-conditioned disks and eluted with 20 mL of EDTA. The strip fractions were counted by LSA (without ^{133}Ba added) and by alpha spectrometry of microprecipitated Ra, as $Ra/BaSO_4$. The data show that 95% of added ^{226}Ra was recovered by the disk from NYC tap water.

Disc Reuse

We examined whether the disks could be reused in order to reduce waste and minimize costs. A single disk was pre-conditioned with 2N Nitric acid, loaded with 106 dpm of ^{226}Ra (from DI water) and stripped with 10 mL of 0.25M EDTA. This loading and stripping procedure was repeated a total of 9 times. We hypothesized that if the crown ether was renewable, it would

1987). Two actinides, Cm and Am were previously found to co-extract with Ra, with extraction efficiencies of 100% and 63%, respectively (Scarpitta 1995, 1996b). The PERALS™ spectrometer, with a 0.250 MeV α-energy resolution, electronically rejects unwanted β/γ signals that may be present in the extracted Ra-bearing organic phase (McDowell and McDowell 1994). We found that PERALS™ could be utilized to measure α-emitting Ra in the 3M strip fraction **only if** EDTA were destroyed by ashing (or precipitating) prior to extraction into RADAEX™. We precipitated EDTA out of solution by adding an equal volume of 16N Nitric acid to a ^{133}Ba spiked water that was allowed to stand in ice for about one hour. The sample was centrifuged and the supernate retained. The EDTA precipitate was washed with cold nitric acid that was then added to the original supernate, following centrifugation. We were able to recover about 85% of ^{133}Ba added to the original EDTA solution. Although not tested, this technique of removing EDTA could be employed if one wished to alpha count the EDTA strip fraction by solid-state alpha spectrometry. Alpha counting at EML (HASL-300, E-Ra-02-07) requires that the sample thickness be $<$ 2 mg cm^2 on 1" diameter Metricil^R filters to minimize α self-absorption.

Finally, we tested whether 3M's Strontium Disks could be utilized to remove any Sr that might be present in a sample intended for LS measurement. It should be noted that the Sr disks were not intended for Radium application. [Note: With Sr Rad disks, Strontium is extracted from aqueous samples, acidified to 2N with HNO_3. After a suitable ingrowth time, ^{90}Y, the progeny of ^{90}Sr, is eluted by washing again with 2N HNO_3 , rather than with EDTA.] We utilized gamma emitting ^{85}Sr and ^{133}Ba as well as ^{226}Ra (with progeny) to make our separate determinations. For each nuclide, we stripped with 0.25M EDTA. The load (DI

water), wash (2N HNO_3) and EDTA strip fractions were LS counted along with the 3M Sr Rad disk (after stripping). The data in Figure 7 show that both Ba and Sr were retained by the Sr Rad disk after loading and washing, since each nuclide eluted with EDTA. We added 440 dpm of ^{226}Ra , in equilibrium with its progeny, to a fresh pre-conditioned Sr disk. Based on the positions and shapes of the spectral peaks, we determined that: (1) 28% of total counts added [^{210}Po + ^{210}Bi] were not retained by the Sr disk, (2) 26% [as ^{226}Ra and ^{210}Pb] were stripped and (3) 31% of total counts added were retained by the Sr disk after EDTA stripping. Although we could not determine the ^{226}Ra progeny retained by the Sr Disk, we concluded that pre-filtering Ra-bearing water through a Sr Rad disk was of little advantage since 80% of added Sr eluted with EDTA.

CONCLUSIONS

Twenty nuclides were individually tested for their retention and elution charactersitics on 3M Empore™ Radium disks. The disk extracted Ra with >95% efficiency. Overall, the disk performed very well, extracting (and eluting) only 3 other divalent elements: Pb, Sr and Ba . The 3 elements that co-eluted with Ra are primarily β or γ emitters whose presence would only interfere with ^{226}Ra determination by LSA. Their presence is of little consequence if one uses an appropriate counting method that measures only α-radiation (^{222}Rn emanation, PERALS™ or α-Spectrometry). Of 6 alpha emitting actinides that were tested, < 6% of added activity eluted in the EDTA strip fraction with <3% remaining on the disk. For 3 transition metals tested, < 5% eluted in the EDTA strip. In certain applications, the disk can be directly counted for ^{226}Ra, using either a gas proportional α/β counter or LS counter, with α-efficiencies of 10%

and 98%, respectively. For QAP applications, either the EDTA strip fraction or the disk itself could be LS counted. Using 3 QAP water samples spiked with 40 dpm of ^{226}Ra, the found to added ratio was 0.90 ± 0.14 by LSA. For potential low-level work, we microprecipitated ^{226}Ra as Ra/BaSO4 from the EDTA strip fraction with > 85% efficiency, using ^{133}Ba as a yield tracer. The use of a primary yield tracer (prior to loading) may not be required if the disk extracts and elutes ^{226}Ra with reproducible efficiency. The disk was not able to extract ^{226}Ra from 50 L of pre-concentrated, filtered NYC tap water because of gram amounts of soluble salts that may have exceeded the capacity of the crown ether. The disk was, however, able to extract 10 dpm of ^{226}Ra added to 2 Liters of un-filtered NYC tapwater with 95% efficiency. The Empore™ Radium disk is effective at separating Ra from other elements and was found to be both a time and reagent saving product suitable for EML's Quality Assessment Program.

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Table 1

Decay Data For Radionuclides Used

Decay Mode

	t-1/2	Beta (MeV)	Gamma (MeV)	Alpha (MeV)	Ionic Radius (Angstom)
H-3	12.33 y	0.019			2.08 (+1)
C-14	5730 y	0.156			2.60 (+4)
Ca-45	163.8 d	0.257			0.99 (+2)
K-40	1.26 E9 y	1.32			1.33 (+1)
Fe-55	2.73 y	pure E.C.			0.64 (+3)
Sr-85	64.84 d		0.514 (100%)		1.13 (+2)
Sr-90	28.5 y	0.546			"
Y-90	2.671	2.28			0.93 (+3)
Ru-106	1.020 y	0.039			0.65 (+4)
Rh-106	29.8 s	3.54 (68%)			0.86 (+2)
Ba-133	10.54 d		0.356 (69%)		1.35 (+2)
Cs-137	30 y	0.514 (95%)	0.662		1.69 (+1)_
Bi-207	30.2 y		0.57(98%); 1.06(77%)		1.20 (+3)
Bi-210	5.01 d	1.160	weak		"
Pb-210	22.3 y	0.060	0.047		1.20 (+2)
Po-210	138.4 d			5.305	-
Ra-226	1600 y		0.186 (4% Rn)	4.78 (95%) + Rn prog	1.40 (+2)
Th-230	8 E4 y			4.68	0.95 (+4)
nat U	*			4.77; 4.20; 4.44	0.89 (+4)
Np-237	2.140 E6 y			4.99 (47%) + Am prog	1.09 (+3)
Pu-242	3.763 E5 y			4.90 (78%)	0.86 (+4)
Am-243	7.380 E3 y		0.076 (60%)	5.27 (88%)	1.06 (+3)
Cm-244	17.6 y			5.76 (24%)	-

* nat U = 48.2% ^{238}U + 49.5% ^{234}U + 2.3% ^{235}U

Data from Browne and Firestone (1986).

Table 2

* LSC RESULTS OF EML's QAP WATER USING EMPORE™ Radium DISKS

	QAP (no Ra) (net cpm)	Sample A (net cpm)	Sample B (net cpm)	Sample C (net cpm)	Mean ± 1 SD	# Found/Added Ratio
2N HNO3 Wash	0	0.3	0.9	0	---	---
net cpm - QAP	---	0.3	0.9	0	0.40 ± 0.46	0.01 ± 0.01
EDTA Strip	7	45.6	36.5	46.2	---	---
net cpm - QAP	---	38.6	29.5	39.2	35.77 ± 5.44	0.895 ± 0.136
Filter post Strip	1.7	6.1	4.1	2.1	---	---
net cpm - QAP	---	4.4	2.4	0.4	2.4 ± 2	0.06 ± 0.05

Components of EML QAP-9603 Water (1.0N HCl)

Gamma	dpm per 20 mL	Mn-54	Co-60	Cs-137			
		51	42	54			
Alpha/Beta	dpm per 20 mL	H-3	Fe-55	Sr-90	Pu-238,239	Am-241	U-nat
		301	99	1.8	2.2	1.0	0.7

#(40 dpm Ra-226 added per 20 mL QAP H2O)

*(50-700 keV ROI in Insta-Gel-XF) 15 min Count : 1 sigma error < 4%

Table 3

Radium in NYC Tap Water Results
(Ra/BaSO4 Microprecipitation)

	* Gross cpm	Counter Efficiency	Ba-133 Yield	dpm Ra-226	mBq L-1
RA-1	0.211	0.35	0.817	0.817	0.30
RA-2	0.056	0.354	0.890	0.178	0.06
RA-3	0.047	0.347	0.686	0.197	0.07
-					
RA-5 (+3.3 dpm Ra)	o.005	0.35	0.929	0.197	und
D.I. Water Blank	0.062	0.218	0.95	0.299	0.10

* No discernable alpha peak on 1" Metricil filters.

The Radium Decay Chains and Principal α/β Energies

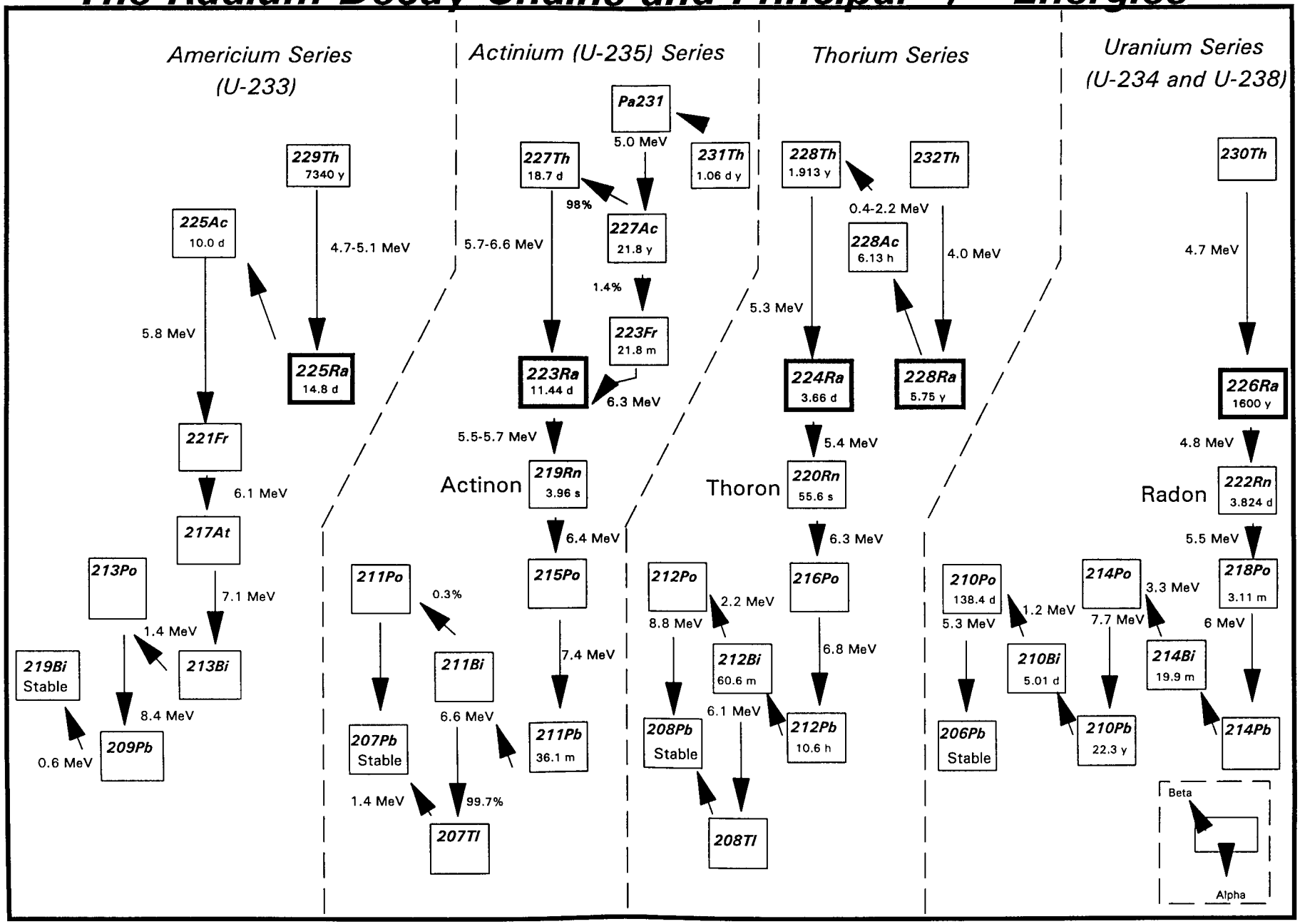


Figure 2

Ra-226 LS Efficiency Calibration Curve

(226Ra + 210Po + 210Bi + 210Pb)

10 mL Insta-Gel + 10 mL Water

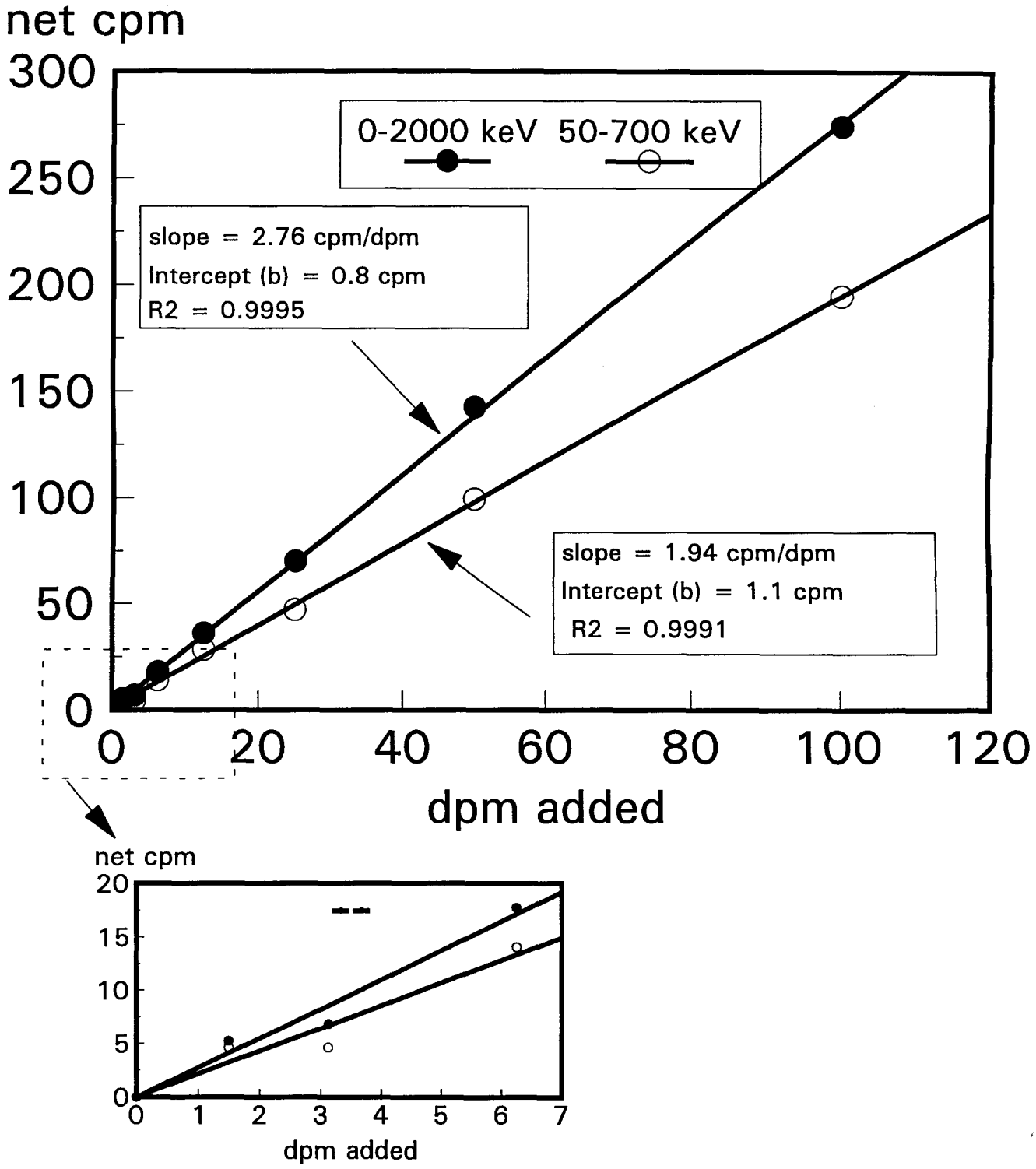
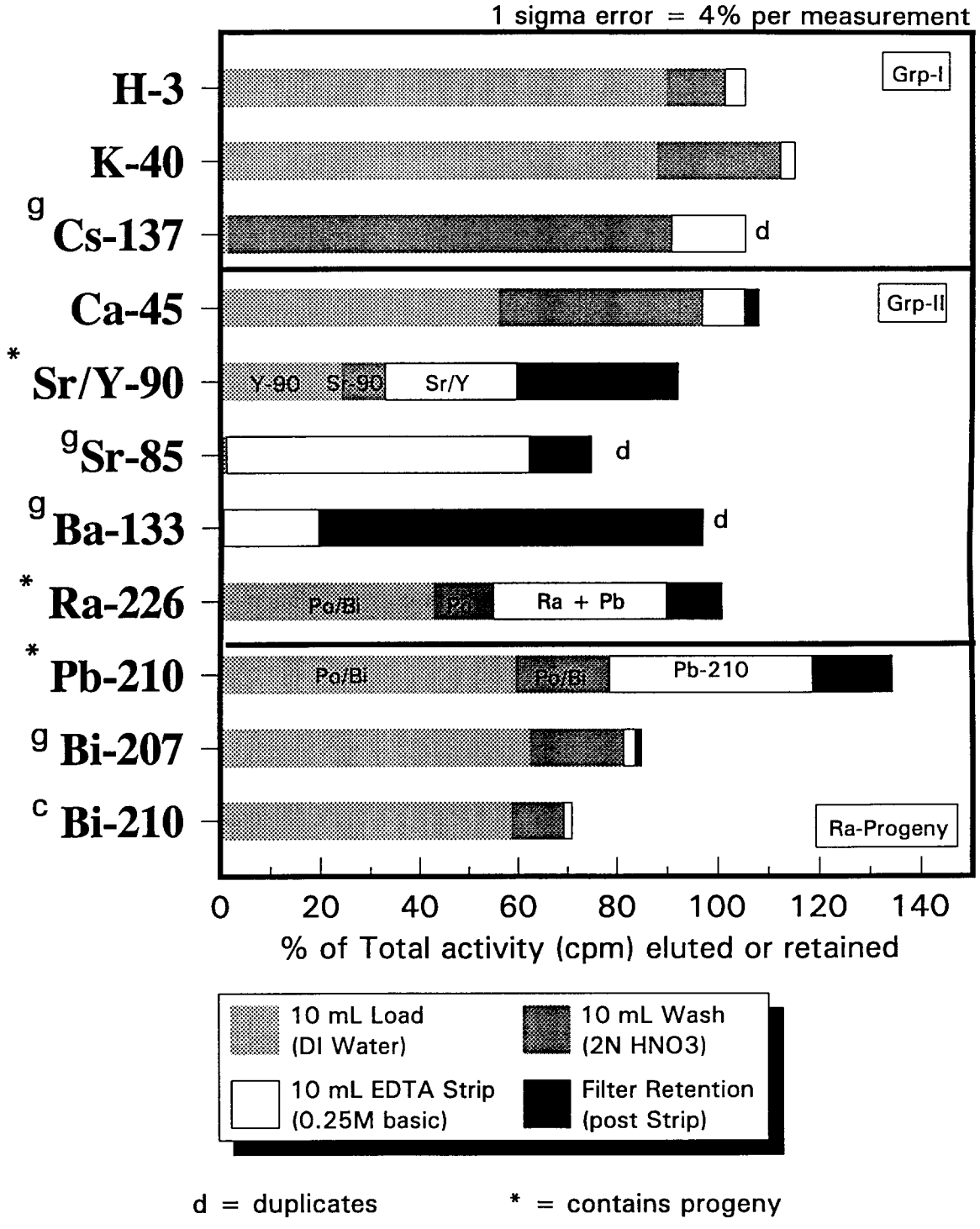


Figure 3a

Behavior of Grp I and II Elememts on Empore™ Ra Disks

LSC, Cerenkov (c) and Gamma (g) Data



d = duplicates

* = contains progeny

Figure 3b

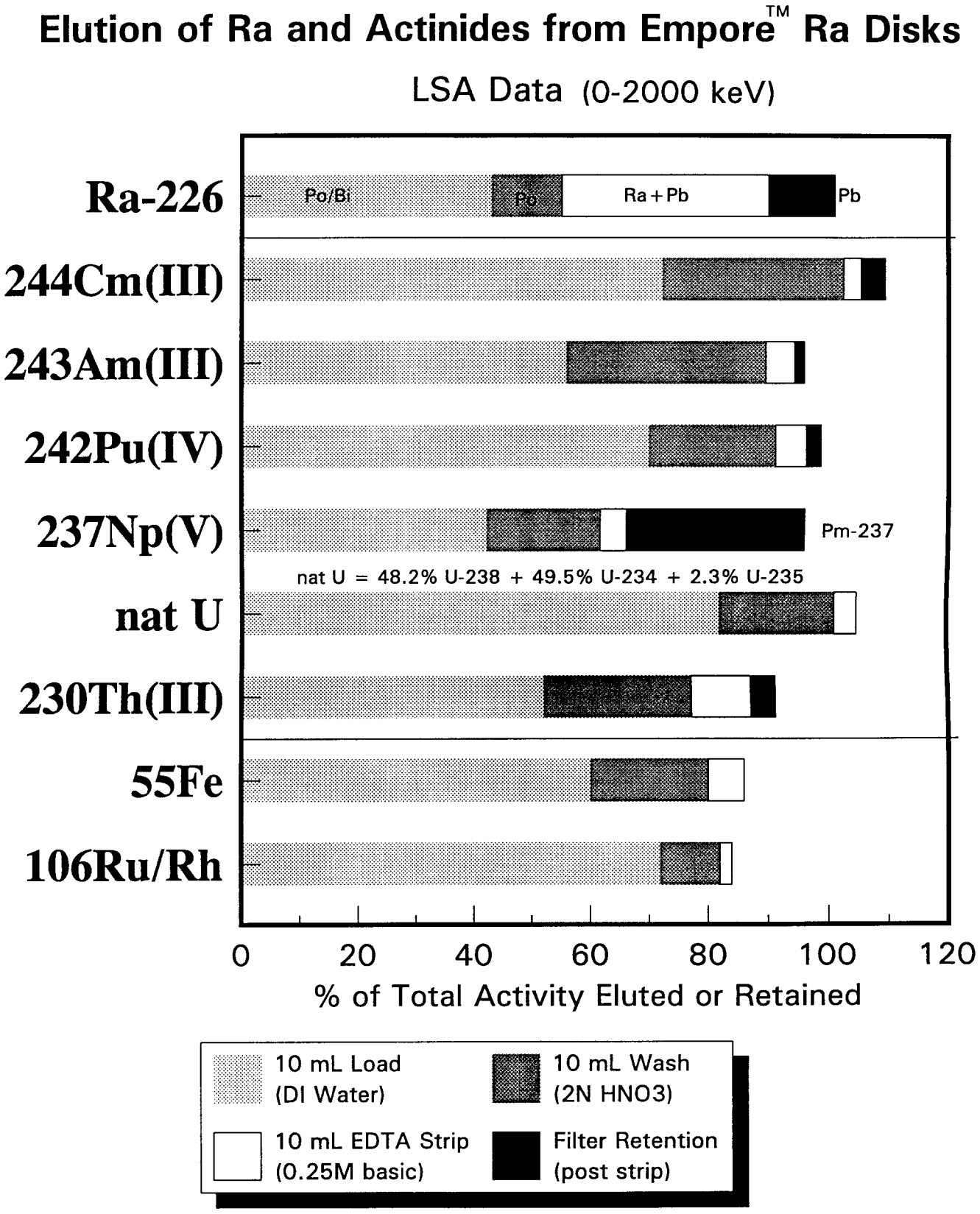
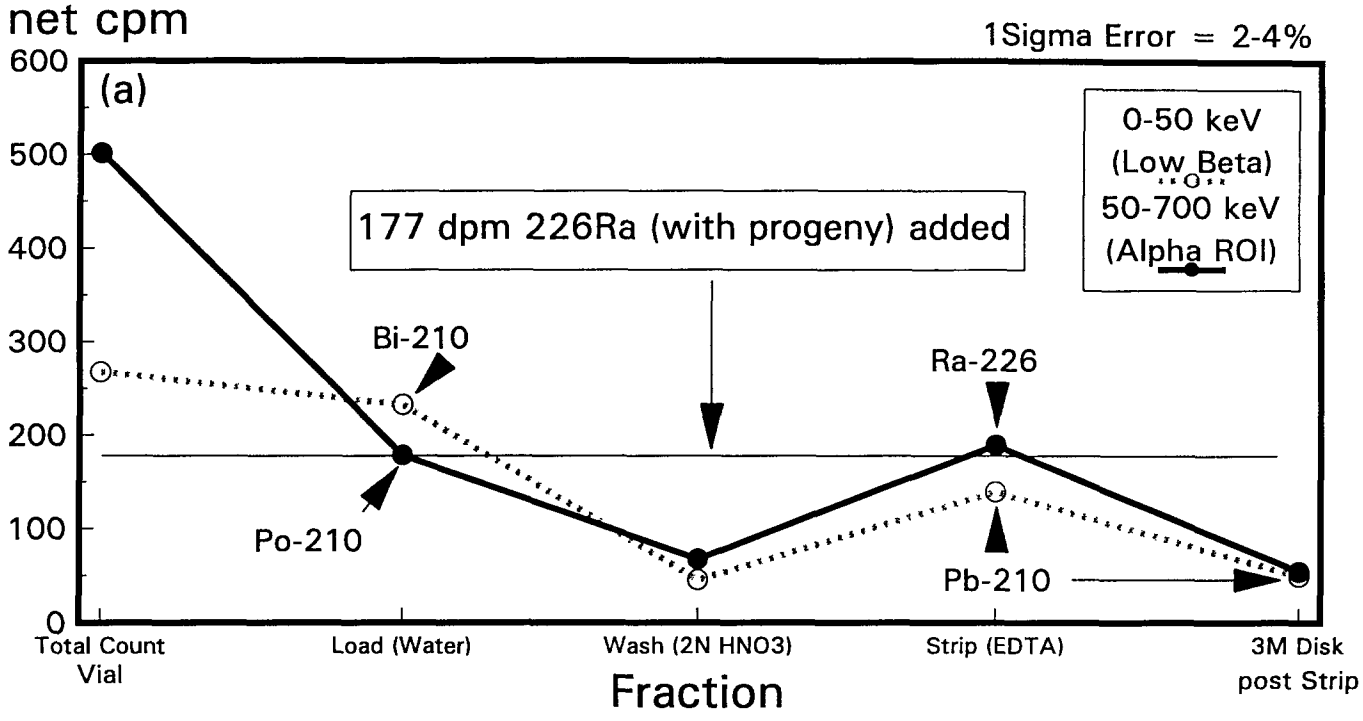

Elution of Ra and Actinides from Empore™ Ra Disks
LSA Data (0-2000 keV)
Ra-226
244Cm(III)
243Am(III)
242Pu(IV)
237Np(V)
nat U
230Th(III)
55Fe
106Ru/Rh
Po/Bi
Po
Ra + Pb
Pb
Pm-237
nat U = 48.2% U-238 + 49.5% U-234 + 2.3% U-235
0
20
40
60
80
100
120
% of Total Activity Eluted or Retained
10 mL Load (DI Water)
10 mL Wash (2N HNO3)
10 mL EDTA Strip (0.25M basic)
Filter Retention (post strip)

Figure 4a,b

LSC Analysis of Empore™ Ra Disk



Empore™ Ra Disk in Insta-Gel-XF after EDTA Strip

10,000 dpm Ra-226 (with progeny) added

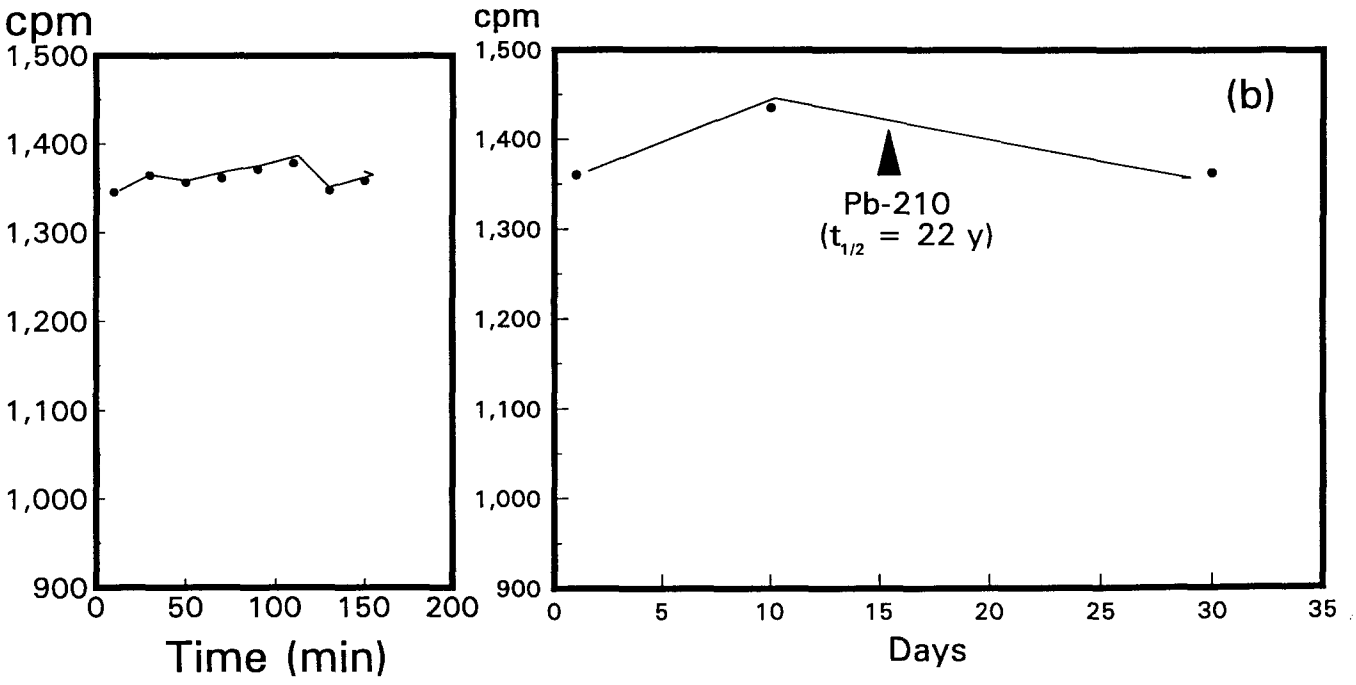


Figure 5

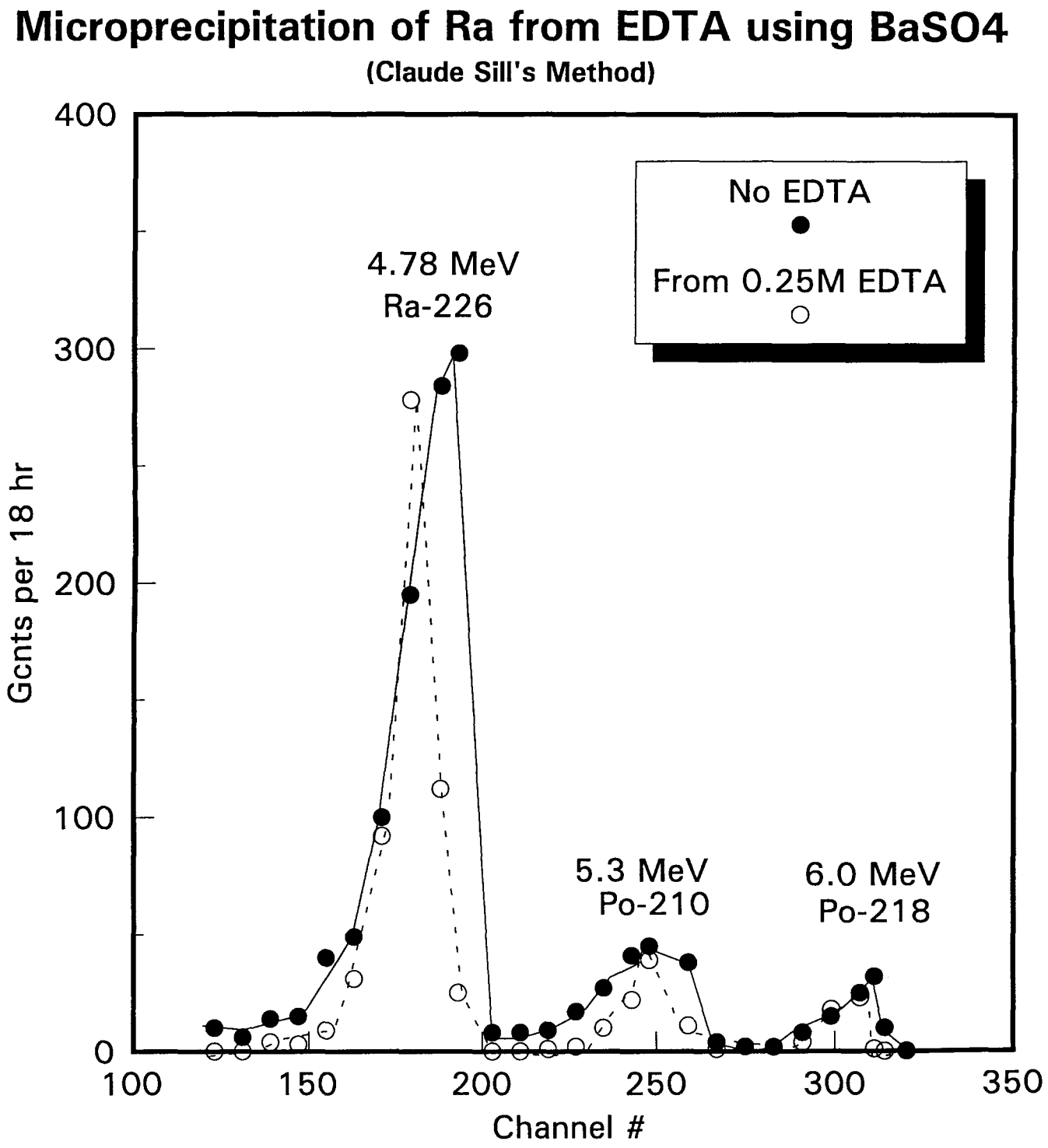
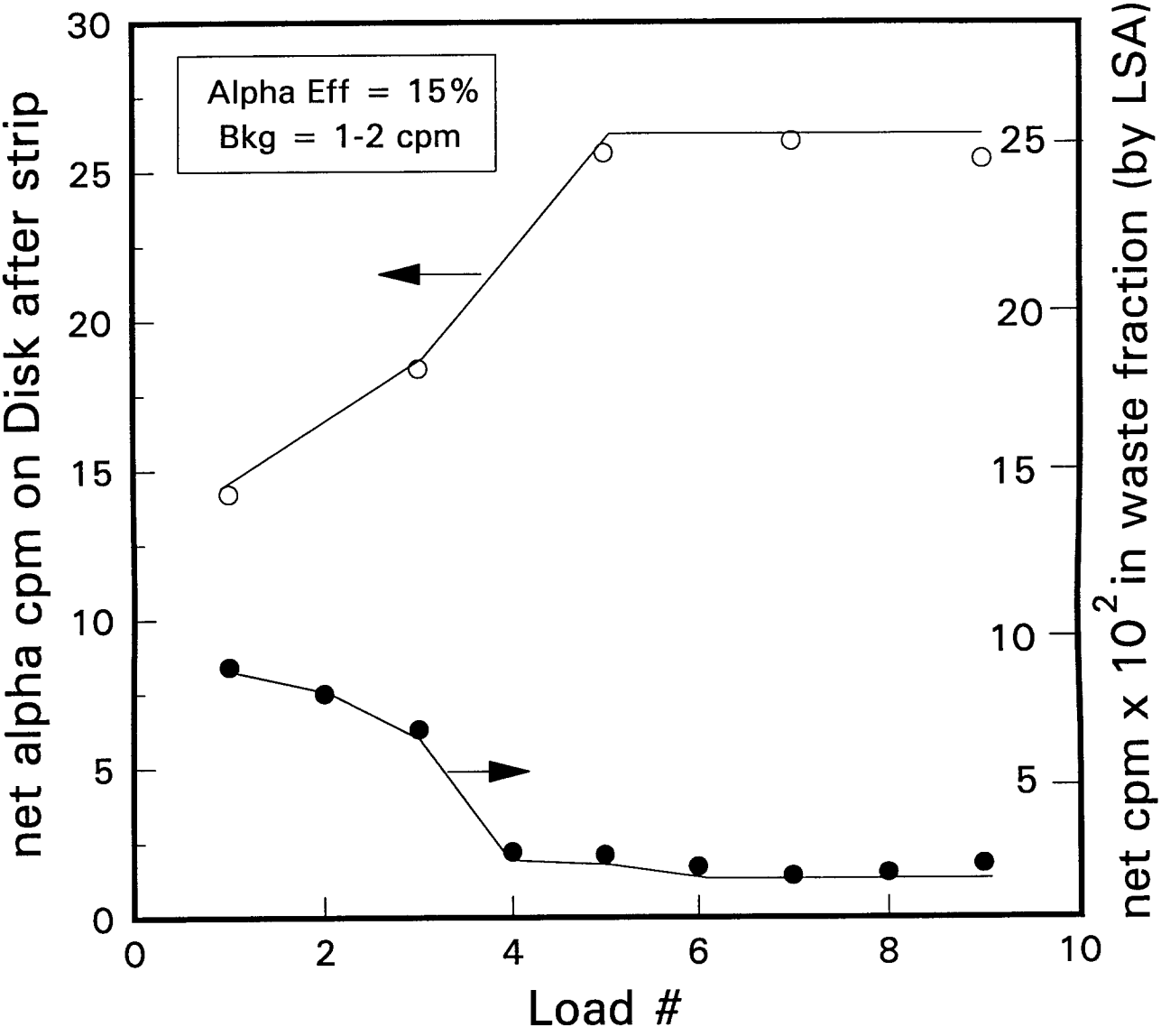

Microprecipitation of Ra from EDTA using BaSO4
(Claude Sill's Method)
No EDTA
From 0.25M EDTA
4.78 MeV
Ra-226
5.3 MeV
Po-210
6.0 MeV
Po-218
Gcnts per 18 hr
Channel #
400
300
200
100
0
100
150
200
250
300
350

Figure 6

Reusability of Empore™ Disk

Gross Alpha and LSA Counts

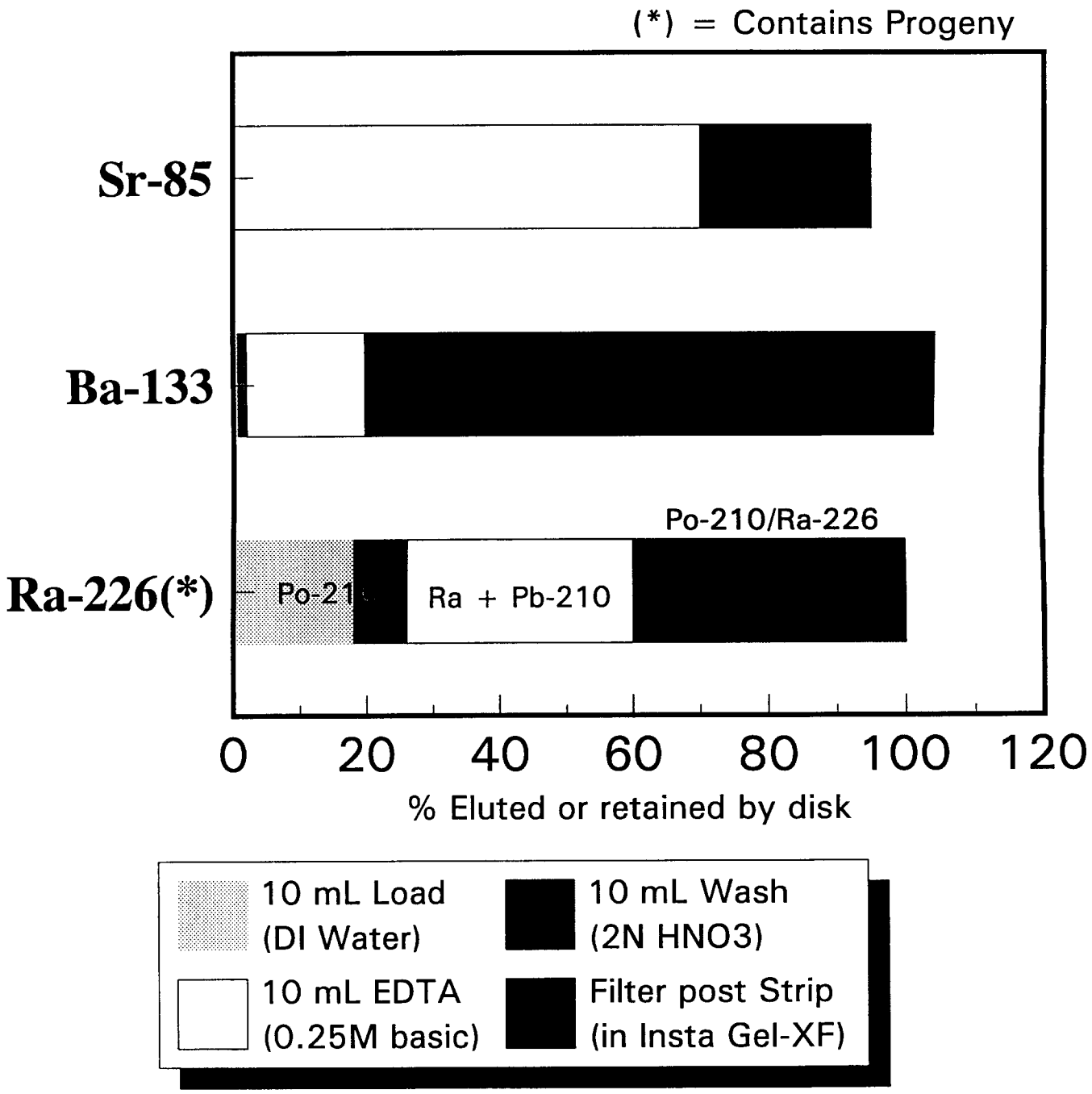


Test Procedure:

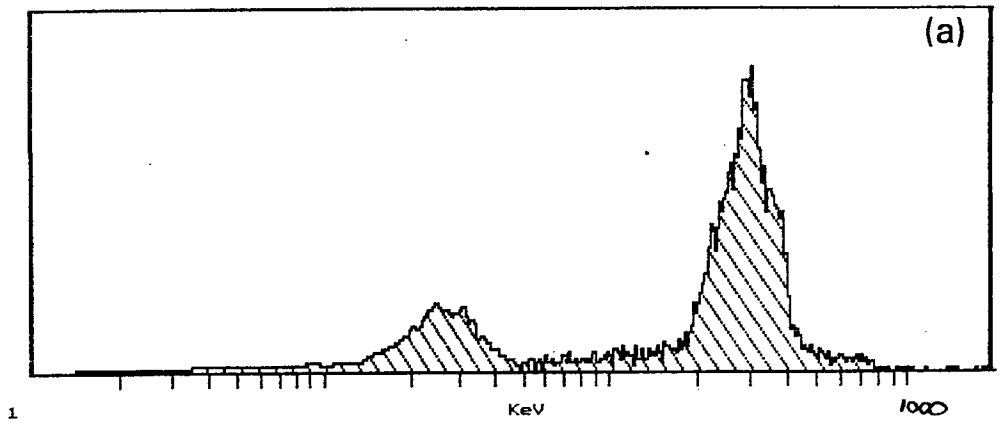
1. 2N HNO3 Wash (10 mL)	3. Waste counted by LSC
2. 106 dpm applied per 5 mL water load	4. 20 mL Strip (0.25M EDTA)

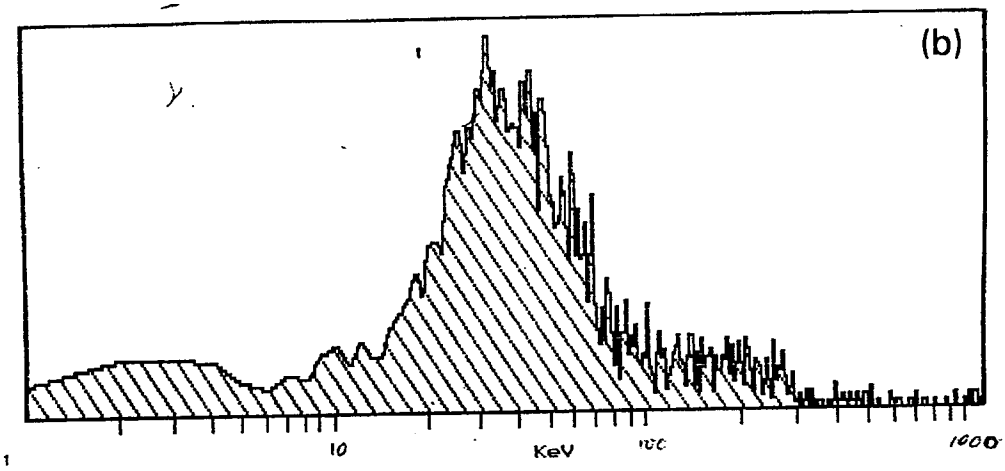
Figure 7

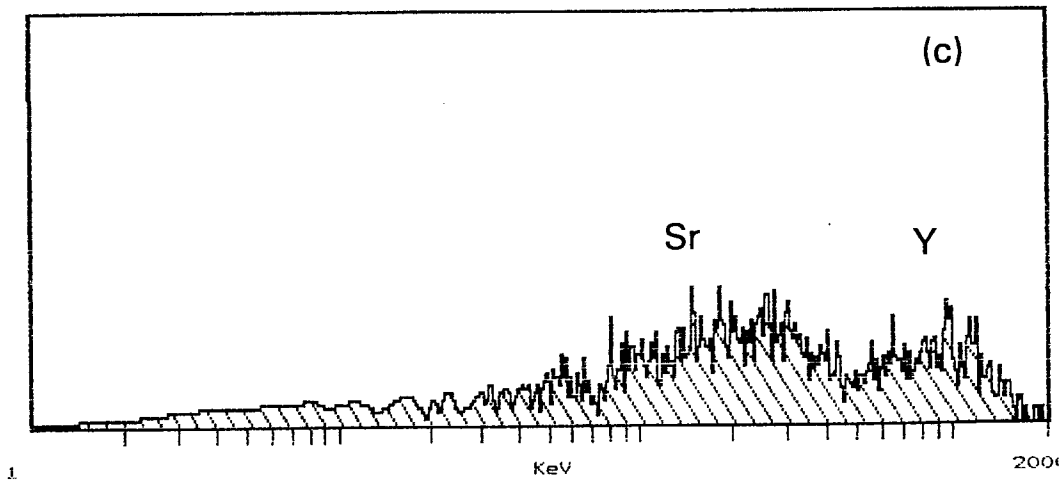
Elution and Retention of 3 Group II Elements Using Empore™ Strontium Rad Disks



Appendix- F1



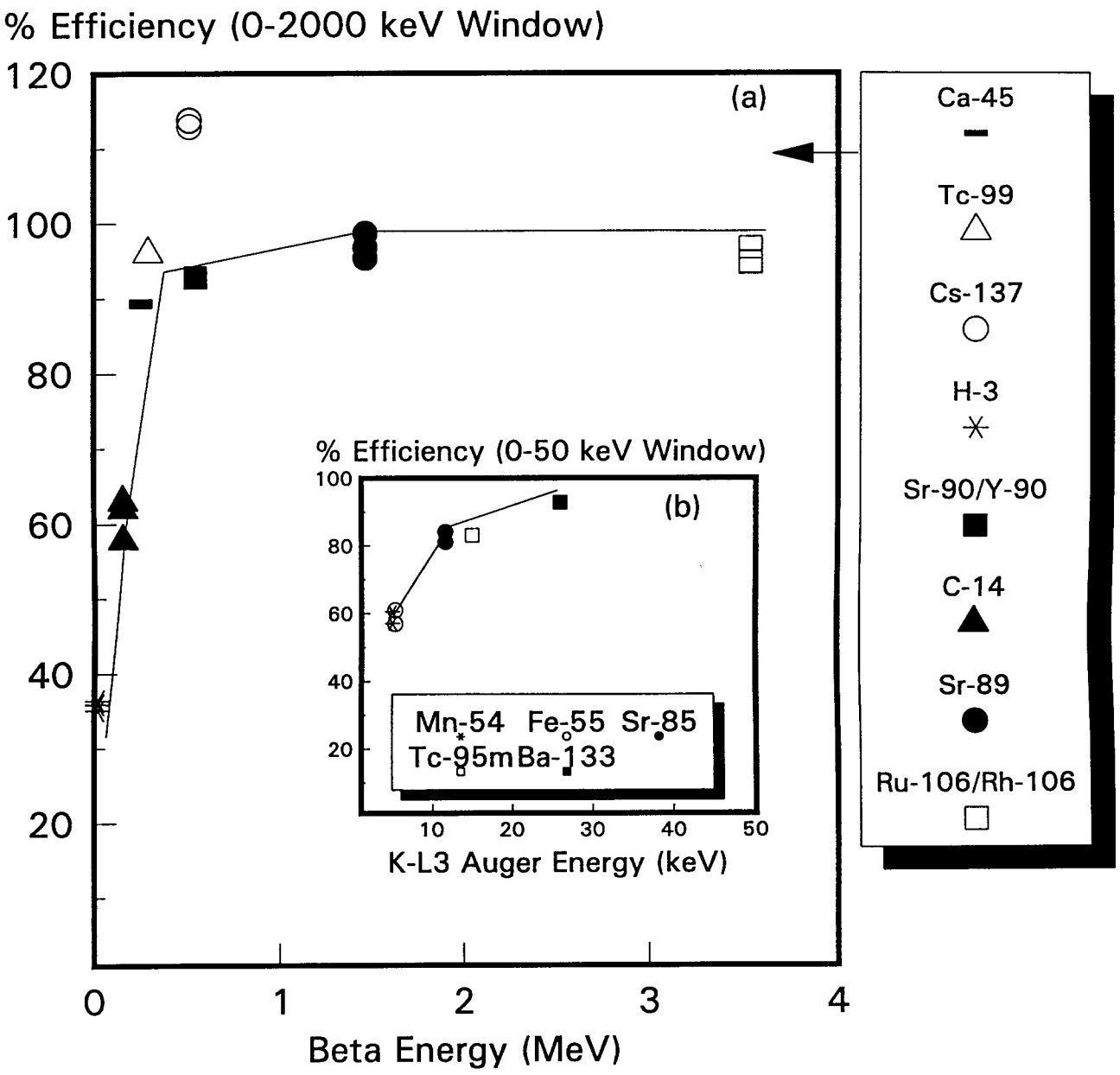




(a) ^{226}Ra + Progeny LSA Spectral Data:

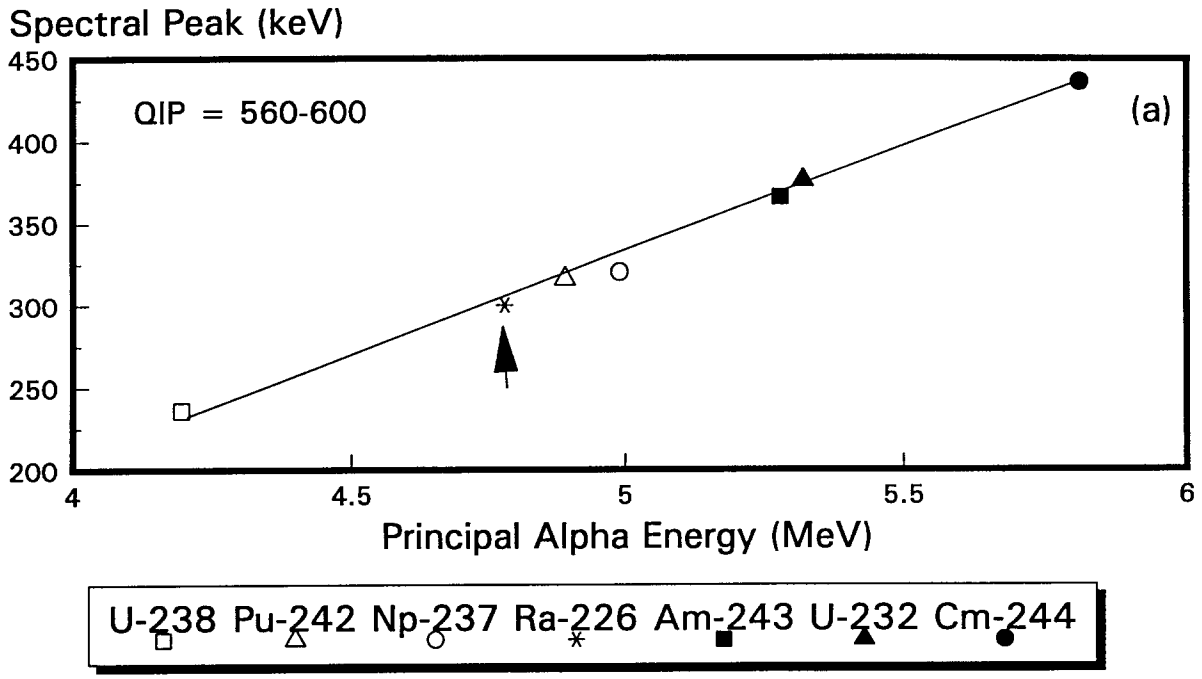
(b) ^{133}Ba LSA Spectral Data: **(c)** ^{90}Sr/Y LSA Spectral Data.

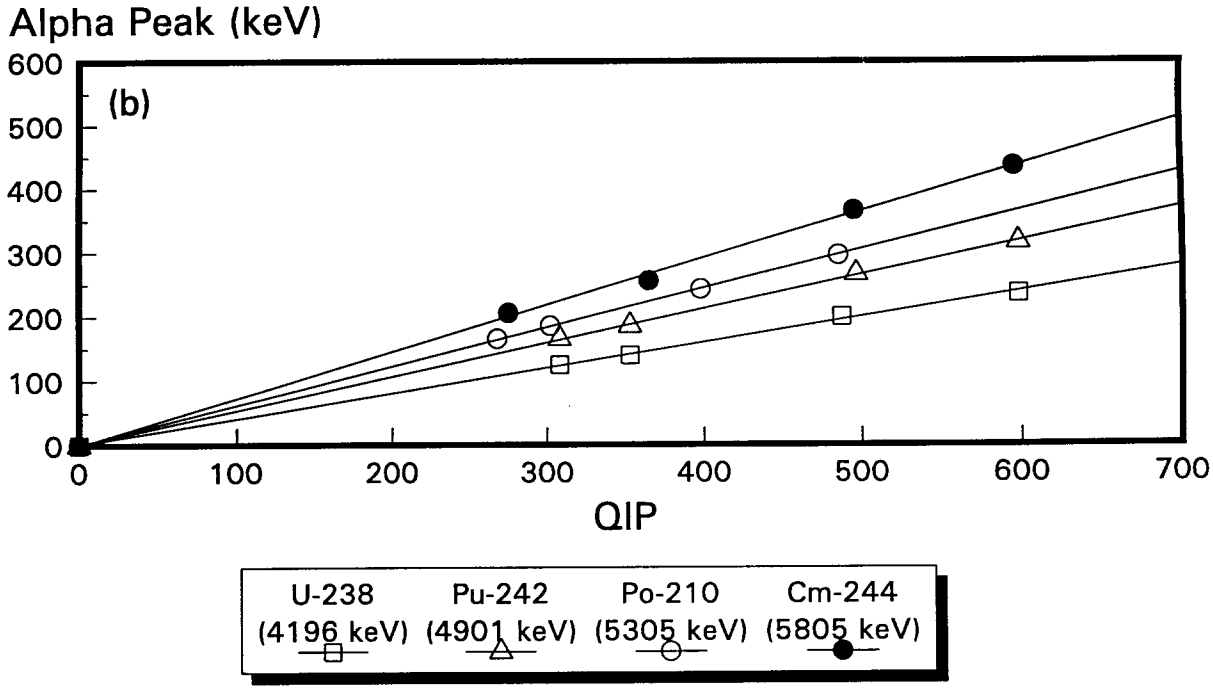
Appendix-F2



Unquenched LS counting efficiencies in 15 mL Insta-Gel using glass vials. (a) beta emitters and (b) gamma emitters. (Data from Scarpitta and Fisenne 1996)

Appendix-F3





Spectral parameters for alpha emitters: Packard Tri-Carb 2250 .
(a) spectal peak vs alpha energy, (b) quench index parameter vs alpha peak.
(Data from Scarpitta and Fisenne 1996)

Apendix-F4

Principal Alpha Energies for Radium and Actinide Series Elements